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Functional Barrier Evaluation of Vibac BOPP Coated Films

Bi-oriented polypropylene film with mineral oil barrier property

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ABSTRACT

The aim of this study is the functional barrier evaluation of plastic films in direct contact with food (primary packaging) versus organic compounds derived from printed cardboard secondary packaging, constituted by recycled paper.
A standard uncoated BOPP film and other different coated films have been tested.
Migration tests were carried out according to European Union plastic Regulation 10/2011, that is, 10 days at 60 °C. The results showed that coating deposition significantly improves the barrier properties of standard polypropylene.

1 INTRODUCTION

Materials intended for food contact use must not transfer any constituents to the food that might endanger human health, change the composition of the food, or cause a deterioration in its organoleptic properties. These requisites contained in Council Directive 10/2011/CE issued by European Commission concern all materials and articles coming into contact with food. [1]

For ecological purposes, cardboard packaging material is largely produced using recycled paper. Recovered paper and board (P & B) may vary in origin and could include paper containing printing inks, adhesives, trace elements, waxes, fluorescent whitening agents and dyes, sizing agents, organochlorine substances, plasticizers, aromatic hydrocarbons, volatile organic compounds, curing and grease-proofing agents, amines, biocides and surfactants. Migration to dry foods was reported for phthalates, diisopropylnaphthalenes (DIPNs), and certain volatile compounds. Paper and board are most often employed in contact with dry solid foods. In this situation substances present in the paper can migrate into the food by direct contact or indirectly through the head-space of the package. Several studies exhaustively show the potential contaminants in recycled paper and board food contact materials [2,3].Moreover, some recent Swiss studies have shown that cardboard boxes made from recycled material contain significant portions of mineral oil [4,5,6.7], the mineral oil stem from printing ink which is commonly used in newspaper printing. If food are packaged in such cardboard boxes, it is possible that mineral oil migrate from the cardboard to the foodstuff. The concentration easily exceed the limit

derived from the Acceptable daily intake (ADI) of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) [8].

Mineral oil saturated (MOSH) consists of linear and branched alkanes; and alkyl-substituted cyclo-alkanes, whilst mineral oil aromatic hydrocarbons (MOAH) included mainly alkyl-substituted polyaromatic hydrocarbons. Products, commonly defined according to their physic-chemical properties, may differ in chemical composition depending on the oil source. The main sources of mineral oil MOH in food are food packaging materials, additives, processing aids and lubricants. These compounds may concentrate in the body after consumption of food stuff, causing organ damages [9].

2 EXPERIMENTAL

2.1 Sample Characteristic

Table n. 1 shows the tested samples.

CML is a std uncoated polypropylene film

VCOAT AA.C, PL.C, AP.C, AL.C, BL.C are coated films produced by Vibac under brand name of

2.2 Analytical methods

2.2.1 Identification and semi-quantitative evaluation of "marker" compounds

The first part of the study is related to the identification of the "marker" compounds to be used for the valuation of the functional barrier of the plastic film intended to come into contact with food.

The analysis is performed by the method described below.

Analysis method: solvent extraction (n-hexane: 10 ml) of 1 dm^2 of sample, addition of the internal standard and GC/MS analysis.

Semi-quantitative evaluation of compounds present in the extraction solvent: using the response factor of the internal standard it is obtained a semi-quantitative estimation of the compounds.

Analytical sensitivity (in regard to the standard): 2 µg/dm^2.

Uncertainty for the applied method: ± 30%.

2.2.2 Expression of the results

The chromatograms obtained in total ion (TIC) and the table with peak identification showed in the results section contain the following information:

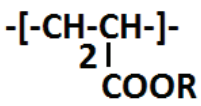
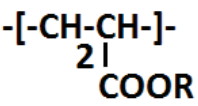
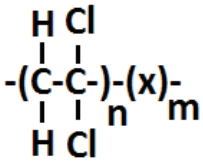
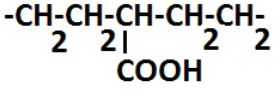
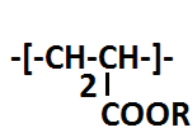
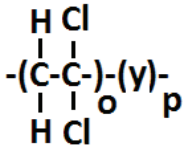
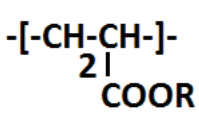
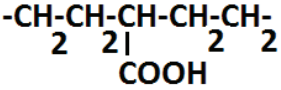
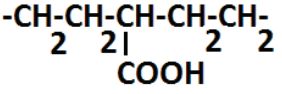
peak retention time (TR)

identification, obtained through the comparison with some mass spectrums and those present in the library (WILEY275K) managed by the analytical system software.

qual. = quality or coincidence index between the sample spectrum and that one in the library (maximum 100 - acceptable > 70).

Semi-quantitative evaluation: methods **are not quantitative**. A **semi-quantitative evaluation** of the concentration is expressed in mg/dm^2 using the internal standard as a reference (also for "not identified" peaks).

Table n. 1

Sample N.	Identification	*Coating on side 1*	*Chemistry*	*Base film*	*Coating on side 2*	*Chemistry*
1	23CML polypropylene base film (uncoated) 23 µm	-		*23CML*	-	
2	25AA.C coated film Acrylic / Acrylic 25 µm	*Acrylic (0,85 g/m²)*		*23CML*	*Acrylic (0,85 g/m²)*	
3	26PL.C coated film PVdC/LTS 26 µm	*PVdC (2,50 g/m²)*		*23CML*	*EAA (0,85 g/m²)*	
4	26AP.C coated film Acrylic / PVdC 26 µm	*Acrylic (0,85 g/m²)*		*23CML*	*PVdC (2,50 g/m²)*	
5	25AL.C coated film Acrylic / LTS 25 µm	*Acrylic (0,85 g/m²)*		*23CML*	*EAA (0,85 g/m²)*	
6	25BL.C coated film Mineral oil barrier / LTS 25 µm	*Functional coating with mineral oil barrier (1,50 g/m²)*	*Acrylate copolymer containing carboxyl groups*	*23CML*	*EAA (0,85 g/m²)*	
7	Printed cardboard constituted by recycled paper					

2.2.3 Functional barrier evaluation

The functional barrier evaluation is performed by a migration test with a solid stimulant. Contact conditions are showed below.

Simulant: poly(2,6-diphenyl-p-phenylene oxide) (MPPO or Tenax), particle size 60-80 mesh, purified by

soxhlet extraction for 3 hours with diethyl ether and conditioning for 3 hours at 160°C.

Contact conditions

Test conditions		**Contact mode**	**Cardboard surface / surface film / mass of Tenax**
Time	Temperature		
10 days	60° C	Cell	1,0 dm^2 / 0,40 dm^2 / 2 g

The samples were conditioned using the appropriate glass cells prepared as follow:

1 dm^2 of cardboard - 0.40 dm^2 of the film (in contact with a specific lacquer side to the Tenax) - 2 g of Tenax. A head space is present between the cardboard and the film. In this way it simulates a box constituted by a secondary packaging (carton: 1 dm^2), a primary packaging (film: 0.40 dm^2) and the edible part simulated by Tenax, that has the function to "adsorb" organic compounds that may derive from cardboard and migrate through the film.

2.2.4 Identification and semi-quantitative evaluation of organic compounds migrated in Tenax

The aim of this analysis is to determine the organic compounds (the compounds identified in the analysis

carried out according to the method described in § 2.2.1) migrated through the packaging material to the simulant Tenax.

Method: the Tenax, previously put into contact with the sample, is extracted with diethyl-ether according to

the norm EN 1186-13 B.

The diethyl ether extract is evaporated in nitrogen and then solubilized with n-hexane, an internal standard (di-propylphthalate) is added. The analysis is carried out by GC/MS.

Data are expressed in micrograms absolute and represent the mass of the compound that is permeated through the film (0.40 dm^2) during conditioning 10 days at 60 °C and adsorbed in Tenax.

Method performances:

detection limit: 2 µg/dm^2 referred to internal standard;

extended uncertainty for the applied method: ± 20%.

2.2.5 Criteria to verify the functional barrier

In the present study we consider that the functional barrier is reached when there is no migration of the compound "marker" in Tenax, that is to say, when the quantity is below the detection limit.

3 RESULTS

3.1 Non volatile organic compounds results – total extract (printed recycled cardboard)

Total ion current chromatogram (TIC): sample 7 (printed recycled cardboard)

Among the compounds identified and semi-quantitatively evaluated, by the analysis of the sample n. 7 described on § 2.2.1, the following have been identified as "markers" of migration.

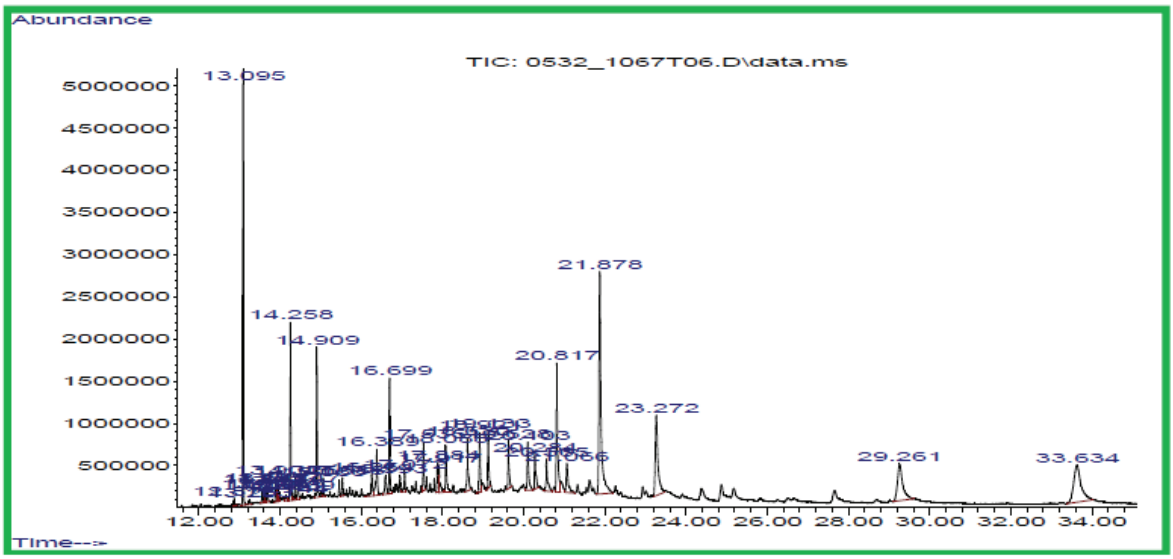


Table n. 2

Peak identification	Coming from	µg/dm²
Iso propyl dodecanoate	Ink	268
Di iso propyl naphtalenes (isomers)	Recycled fiber	54 sum
Di propyl phthalate (internal standard)	Internal standard	100
Di iso butyl phatalate	Adhesive and recycled fiber	92
Bis 2-ethylhxyl maleate	Ink	76
Linear saturated aliphatic hydrocarbons from n-C16 to n-C25	Recycled fiber and ink	200 sum
Linear saturated aliphatic hydrocarbons from n-C26 to n-C30	Recycled fiber and ink	228 sum
Di 2-ethylhexil phatalate	Adhesive and recycled fiber	95
Glycerol tricaprylate	Ink	1176 sum
Benzophenone *Compound added to cardboard*	Photoinitiator used in UV printing	550

3.2 Results in the determination of organic compounds migrated Tenax through the film sample

As described in §2.2.4, the functional barrier has been evaluated through the analysis of the products migrate into the Tenax.

Table n. 3

Marker Compound	**TR**	**qual**	***Total amount in cardboard (µg/dm²)***	**Migration in Tenax 10 days at 60 °C (µg)**					
			Printed cardboard	CML	AA.C	PL.C	AP.C	AL.C	BL.C
			Sample 7	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Di propyl phthalate (internal standard)	14.25	90	*100*	25	25	25	25	25	25
Iso propyl dodecanoate	13.09	90	*268*	106	73	6	8	22	4
Di iso propyl naphtalenes (isomers)	From 13.56 to 13.95	> 90	*54 sum*	30 sum	19 sum	< 5 sum	< 5 sum	< 5 sum	< 5 sum
Di iso butyl phatalate	15.41	91	*92*	4	5	<2	<2	<2	<2
Bis 2-ethylhxyl maleate	16.69	90	*76*	<2	<2	<2	<2	<2	<2
Linear saturated aliphatic hydrocarbons from n-C16 to n-C25	From 12.87 to 18.50	> 90	*200 sum*	35 sum	16 sum	<10 sum	< 10 sum	< 10 sum	< 10 sum
Linear saturated aliphatic hydrocarbons from n-C26 to n-C30	From 19.13 to 30.00	> 90	*228 sum*	<10 sum	<10 sum	<10 sum	<10 sum	<10 sum	<10 sum
Di 2-ethylhexil phatalate	19.42	86	*95*	<2	<2	<2	<2	<2	<2
Glycerol tricaprylate	From 20.81 to 29.79	-	*1.176*	<10 sum	<10 sum	<10 sum	<10 sum	<10 sum	<10 sum
Benzophenone*	13.21	90	*550*	89	46	20	4	17	3

**Compound added to cardboard*

Table n. 4

"Marker"	CML Sample 1	AA.C Sample 2	PL.C Sample 3	AP.C Sample 4	AL.C Sample 5	BL.C Sample 6
Iso propyl dodecanoate	39,6	27,2	2,2	3,0	8,2	1,5
Benzophenone	16,2	8,4	3,6	0,7	3,1	0,5
Di iso propyl napthelenes (isomers)	55,6	3,5	-	-	-	-
Di iso butyl phtalate	4,4	5,4	-	-	-	-
Bis 2-ethylhexyl maleate	-	-	-	-	-	-
Linear saturated aliphatic hydrocarbons from n-C16 to n-C25	17,5	8,0	-	-	-	-
Linear saturated aliphatic hydrocarbons from n-C26 to n-C30	-	-	-	-	-	-
Di 2-ethylhexyl phtalate	-	-	-	-	-	-
Glycerol tricaprylate	-	-	-	-	-	-

Table n. 4 shows data migration in Tenax of these compounds, expressed as % of each compound migrated through 1 dm^2 (size of the sample used in setting the test) versus the qty contained in the sample n. 7 (printed recycled cardboard).

Since the migration has been accelerated by increasing the temperature, applying the Arrhenius equation, we can estimate the duration of functional barrier at room temperature.

$t2 = t1*Exp((-Ea/R)*(1/T1-1/T2))$ [10]

t2:Testing time

t1: contact time

Ea: activation Energy (worst case 80 kJ/mol [11])

R: 8.31 J/(K mol)

T1: contact temperature in Kelvin

T2: testing temperature in Kelvin

The below table shows the correlation between 60 °C and different temperatures.

The results measured after 10 days at 60 °C are equivalent to the results after 300 days at 25 °C.

Table n. 5

	Acceleration related to		
Test temperature	20 °C	25 °C	40 °C
60 °C	46	30	6

4 CONCLUSIONS

From the data shown in Table n. 3 and in accordance with the criteria defined in § 2.2.5, we observed as follows:

The films PL.C (n.3), AP.C (n.4), AL.C (n.5) and BL.C (n.6) are functional barriers to **compounds such as diisopropyl naphthalenes, diisobutyl phthalate, linear saturated aliphatic hydrocarbons from n-C16 to n-C30**, while the BOPP uncoated film (sample n. 1) and the BOPP film coated acrylic/acrylic (sample n. 2) are NOT functional barriers.

All the films analysed are functional barriers to the **compounds bis 2-ethylhexyl maleate, 2-ethylhexyl phthalate, and glycerol tricaprylate**.

All the films are not functional barriers **to Isopropyl dodecanoate compounds and benzophenone**, even though the migration data, detected for films n. 3, 4, 5 and 6, are lower than those of uncoated BOPP film (sample n. 1) and BOPP film coated acrylic/acrylic (sample n. 2).

BL.C (Mineral oil barrier coating/LTS – sample n. 6) shows the best results.

5 REFERENCE

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